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54 **Process of preparing tantalate x-ray intensifying phosphors with improved efficiency.**

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Description**FIELD OF THE INVENTION**

5 This invention relates to a process for preparing luminescent phosphor materials. More particularly this invention relates to a process for preparing X-ray intensifying phosphors with improved efficiency.

BACKGROUND OF THE INVENTION

10 X-ray intensifying screens are generally used in conjunction with silver halide photographic films and serve to enhance the image formed on that film. Phosphors, which are the active component of X-ray screens, are legion in number and include the tungstates, the oxysulfides, and the oxybromides, among others.

Particularly efficient phosphors which may be used in the preparation of an X-ray intensifying screen are the tantalates described by Brixner in U.S. Patent 4,225,653 (corresponding with EP-A-0 011 909). These phosphors are based on yttrium, lutetium, and gadolinium tantalates of the M' monoclinic form and are generally activated with rare earths such as terbium, thulium and niobium, for example, as well described in the aforementioned reference. Since these phosphors have a high X-ray stopping power, they are presently widely used for the preparation of these intensifying screens and the method for their
20 preparation includes the mixing of ingredients followed by firing this mixture to form the phosphor crystal lattice itself.

During this firing step it is often beneficial to use a flux which usually forms a partial liquid at the elevated temperatures commonly used. Thus, the flux can be thought of as a fluid in which the various component parts of the phosphor react to form the phosphor. These fluxes are generally alkali metal salts which are then removed from the reaction mixture by washing. Commonly known fluxes include: Li_2SO_4 ,
25 pure LiCl , BaCl_2 , SrCl_2 , and mixtures of two of these salts, for example. Some fluxes are better to use than others since at the elevated temperature in which the phosphor is fired, some of the halide salts will vaporize and corrode the equipment. Lithium sulfate may decompose at these temperatures to give lithium oxide and oxides of sulfur. Lithium oxide is very reactive and can form lithium tantalate and/or lithium
30 niobate in the phosphor oxide mixture. Lithium tantalate and niobate, however, are not as efficient as, for example, the yttrium compounds when used as X-ray phosphors. Thus, there is a need to find better flux systems for the preparation of X-ray intensifying phosphors.

The use of a rare earth oxide phosphor containing alkali metal silicates and germanates, is also known. In this particular case, however, the silicate is used as an integral mixture with the phosphor itself and it is
35 reported that the brightness of the rare earth oxide phosphor is increased. The phosphors produced by this technique are not X-ray intensifying phosphors, but are red-emitting phosphors used in cathode ray tubes, for example.

It is an object of this invention to provide a tantalate phosphor of the M' monoclinic form with improved phosphor efficiency and purity which are achieved by reducing the level of contaminants in the phosphor
40 reaction mixture.

SUMMARY OF THE INVENTION

In accordance with this invention there is provided a process for preparing a phosphor with improved X-ray efficiency and purity prepared from a tantalate phosphor having the monoclinic M' structure selected
45 from the group consisting of:

- (a) $\text{YNb}_x\text{Ta}_{1-x}\text{O}_4$, where x is 0 to 0.15;
- (b) $\text{LuNb}_x\text{Ta}_{1-x}\text{O}_4$, where x is 0 to 0.20;
- (c) $\text{Y}_{1-y}\text{Tm}_y\text{TaO}_4$, where y is 0 to 0.03;
- 50 (d) a solid solution of (a) and (b);
- (e) a solid solution of (a) and (c);
- (f) $\text{Y}_{1-y}\text{Tb}_y\text{TaO}_4$, where y is 0.001 to 0.15;
- (g) $\text{Lu}_{1-y}\text{Tb}_y\text{TaO}_4$, where y is 0.001 to 0.15;
- (h) $\text{Gd}_{1-y}\text{Tb}_y\text{TaO}_4$, where y is 0.001 to 0.15;
- 55 (i) a solid solution of at least two of (f), (g) and (h);
- (j) any of (a) to (i) wherein up to 45 mole percent of the yttrium, lutetium or gadolinium is replaced by lanthanum;

(k) any of (a) to (i) wherein up to 15 mole percent of the yttrium, lutetium or gadolinium is replaced by ytterbium; and

(l) any of (a), (b), (c), (d) and (e) wherein up to 15 mole percent of the yttrium or lutetium is replaced by gadolinium;

5 the process comprising

(a) intimately mixing stoichiometric quantities of corresponding precursor oxides;

(b) mixing the resultant mixture with a flux capable of producing an alkali metal oxide;

(c) firing the flux-containing mixture in an inert container in the range of 1100 °C to 1400 °C for at least 3 hours; and

10 (d) recovering the phosphor;

characterized in that the flux of step (b) also contains 0.1 to 1.0% of an alkali metal metasilicate.

BRIEF DESCRIPTION OF THE DRAWINGS

15 The accompanying Figures form a material part of this disclosure wherein:

FIG. 1 is a plot of screen coating weight vs. relative speed of the phosphor prepared using a flux of the prior art, A, and the flux of this invention, B, for terbium activated yttrium tantalate.

FIG. 2 is a plot similar to FIG. 1 but using thulium activated yttrium tantalate phosphor.

FIG. 3 is a plot similar to FIG. 1 but using niobium activated yttrium tantalate phosphor.

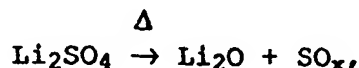
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DETAILED DESCRIPTION OF THE INVENTION

FIG. 1 shows a plot of terbium activated yttrium tantalate phosphor prepared with a standard flux and with a flux containing an effective amount of an alkali metal metasilicate therein. These plots wherein Curve A is the standard, conventionally prepared phosphor and Curve B represents the phosphor prepared by the process of this invention are shown in Relative Speed vs. X-ray Screen Coating Weight (g /in²). FIG. 2 is similar to FIG. 1 except for using a thulium activated yttrium tantalate phosphor, while FIG. 3 is similar to FIG. 1 except for the use of niobium activated yttrium tantalate phosphor. All of these plots show the improved efficiency that can be obtained using the process of this invention vs phosphor prepared without the addition of the metasilicate to the firing flux.

The M' monoclinic tantalate phosphors of this invention are preferably prepared as described in Brixner U.S. Patent 4,225,623, the disclosure of which is incorporated herein by reference. Thus, during the conventional manner for preparing a tantalate phosphor, stoichiometric amounts of the various oxides are usually blended to form an intimate mixture. This blending may be accomplished in a number of conventional ways. For example, the ingredients may be ball-milled or simply shaken together in some sort of blender. The use of a liquid medium to improve the efficiency of the mixing process such as water, fluorochlorinated hydrocarbons or other such inert fluids, may also be incorporated. Then, to make the X-ray intensifying phosphor of this invention, this mixture of ingredients is also mixed with a suitable flux in which an effective amount of an alkali metal metasilicate is also incorporated. While not being limited to any particular theory, the presence of the alkali metal metasilicate is believed to be a critical member of the flux combination of this invention as attested, for example, by the following reaction which occurs during decomposition of an alkali metal sulfate, e.g., Li₂SO₄, a common flux used in the preparation of tantalate phosphors.

45



50 where x is 2 or 3



It is believed that the addition of alkali metal metasilicate to the flux sequesters alkali metal oxide which may be formed in the course of the firing reaction. After firing in the conventional manner flux and soluble reaction products are removed by water leaching. The luminescent product which has the selected particle size is a tantalate of the M' monoclinic variety is then recovered and is useful for the preparation of an X-ray intensifying screen.

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As mentioned previously, there are a host of fluxes capable of producing an alkali metal oxide which can be used to prepare the phosphor described above. These include the alkali metal, e.g., lithium, sodium and potassium, sulfates, phosphates, carbonates. The total flux is present in the reaction mixture in 30% to 60% by weight, preferably 45% to 55% by weight, based on the total weight of oxide (phosphor starting material). The alkali metal, e.g., lithium, sodium, potassium, metasilicate component of the flux is present in an amount of 0.1% to 1.0%, preferably 0.2% to 0.6% by weight, based on the total weight of phosphor starting material. A particularly preferred flux is Li_2SO_4 . To the flux capable of producing an alkali metal oxide is added the alkali metal metasilicate, preferably lithium metasilicate. The mixture of phosphor starting materials, flux with alkali metal metasilicate can be fired, e.g., for at least three hours, at elevated temperatures from 1100°C to 1400°C, before washing to remove the flux and recovering the phosphor. A preferred temperature range is from 1250°C to 1300°C.

After the intensifying phosphor is made according to the teachings of this invention, it may be dispersed in any of the commonly known binders, e.g., polyvinyl butyral or the acrylates or methacrylates, using a solvent, e.g., an alcohol, chlorinated hydrocarbon, ketone or butyl acetate. Small amounts of fumed silica may be present in the phosphor to enhance handling and make the phosphor easier to pour. After dispersing in the binder, the phosphor is then cast on a conventional support, e.g., cardboard, polyester film or thin metal sheets. A brightener may also be present within the phosphor and various reflective materials may be present as an underlayer or within the support itself to enhance the generation of light when the phosphor is struck by X-radiation. TiO_2 dispersed in a binder and cast on the support is conventional as well as the use of small particles of rutile TiO_2 directly in a film support. All of these procedures are well-known in the art. Over the phosphor layer which has been cast on the support, a conventional protective topcoat may be applied. These topcoats are also well-known in the prior art and serve to protect the rather expensive phosphor layer from stains and defects during the handling thereof. Conventional supports, binders, mixing and coating processes for the manufacture of typical X-ray intensifying screens are, for example, described in Patten U.S. Patent 4,387,141.

It is conventional to use the intensifying phosphors of this invention as X-ray intensifying screens. These are usually used in pairs in cooperation with double-side coated medical X-ray silver halide photographic film elements, although it is sometimes common to use single-side coated silver halide photographic film elements for some applications. A pair of screens is conventionally used and the coating weights of each screen may be different, if required. Thus, an asymmetric pair of screens can be used to get the best results. Medical X-ray evaluations represent the commercial use for the phosphor of this invention cast into an X-ray intensifying screen. A dimensionally stable, polyethylene terephthalate film support into which small amounts of rutile or anatase titanium dioxide have been incorporated is the preferred support for the phosphor of this invention.

EXAMPLES

This invention will now be illustrated by the following specific examples wherein the percentages and parts are by weight:

EXAMPLE 1

A mixture of 1 mole of tantalum oxide, 0.997 mole yttrium oxide and 0.003 mole of terbium oxide were thoroughly blended with a mixture of 49.5% of lithium sulfate and 0.5% of lithium metasilicate. The flux is present in an amount of 50% based on the total weight of oxide. This mixture was then fired at 1290°C in air for 12 hours. The lithium salts were then washed from the resultant phosphor with deionized water. After drying, the phosphor was treated by the addition of 0.0002 g of fumed silica per g of phosphor to improve the flowability thereof. The phosphor is then dispersed by ball-milling 100 g of the phosphor in 6 g of a carboxylated methyl methacrylate acrylic binder with 1 gm of a mixture of a block copolymer of polyoxyethylene and polypropylene glycol, a plasticizer, and dioctyl sodium sulfosuccinate, wetting agent, using a solvent mixture of a 1 to 1 weight mixture of n-butyl acetate and n-propanol. This suspension was coated on 0.25 mm (0.010 inch) polyethylene terephthalate with about 5 mg/cm² TiO_2 dispersed therein. The dispersion was coated at various coating weights and the effect on speed tested by exposure to an X-ray source at 70 kV peak and 5 mAs at a photographic X-ray film to X-ray tube distance of 130 cm. Relative speeds obtained are shown in Curve B of FIG. 1. For control purposes, a similar screen was made using only a lithium sulfate salt as the flux. The relative speed results are shown by Curve A of FIG. 1. These results show that the phosphor prepared with the flux of this invention will have higher relative speed than that prepared with a single, conventional flux.

EXAMPLE 2

A mixture of 1 mole of tantalum oxide, 0.997 mole of yttrium oxide and 0.003 mole of thulium oxide were blended with the same flux described in Example 1 using the same conditions. Screens were made by coating the washed and dried phosphor on the support described in Example 1. Samples at various coating weights were tested by exposure to photographic films also as described in Example 1. The results, for the phosphor of this invention are shown in Curve B. In Curve A the results of a control using a standard, single flux, are plotted.

EXAMPLE 3

Another sample of phosphor was prepared in the same manner as described in Example 1. This phosphor was prepared from 0.98 mole of tantalum oxide, 0.02 mole of niobium oxide and 1 mole of yttrium oxide. After firing, washing, drying, blending with a binder and coating at various coating weights on a support, samples of the coatings were used to expose photographic films. The results are shown in FIG. 3 as Curve B while that of a control using a standard, single flux, made at the same time as the invention phosphor is plotted as Curve A.

EXAMPLE 4

A mixture of 678.2 gm yttrium oxide, 1313.8 gm tantalum oxide and 8.0 gm niobium oxide were mixed in a vibro-rotary mill using alumina cylinders and Freon® TF, E. I. du Pont de Nemours and Co., Wilmington, DE, as the milling fluid. The oxide mixture was dried and combined with a flux mixture consisting of 950 g lithium sulfate and 50 g lithium metasilicate. As a control, a 2000 g mixture of oxides was blended with 1000 g of lithium sulfate. These mixtures were placed in high purity alumina crucibles, heated to 1290 °C and held at this temperature for 12 hours. After the crucibles had cooled to near room temperature, the fired masses were removed from the crucibles and washed with deionized water until the water tested free of lithium sulfate. The water was removed by filtration and the phosphors were dried. The phosphors were dispersed in a solution of acrylic polymers, wetting agents and solvent as described in Example 1. The phosphor dispersions were coated on reflective substrates so as to give X-ray intensifying screens with various coating weights. The screens were exposed to X-rays as described above and the following results were obtained as shown in the Table below:

Table

Screen Speed for Various Fluxes		
Screen coating Weight	Lithium Sulfate	Lithium Sulfate/Lithium Metasilicate
2.58 g/cm ² (0.4 g/sq in)	1.00	1.01
3.23 g/cm ² (0.5 g/sq in)	1.08	1.14
3.87 g/cm ² (0.6 g/sq in)	1.10	1.24

As can be seen from these results, the addition of an alkali metasilicate to the flux results in higher phosphor efficiency. This will mean lower exposure of patients to X-radiation.

Claims

1. A process for preparing a phosphor with improved X-ray efficiency and purity prepared from a tantalate phosphor having the monoclinic M' structure selected from the group consisting of:

- (a) $\text{YNb}_x\text{Ta}_{1-x}\text{O}_4$, where x is 0 to 0.15;
- (b) $\text{LuNb}_x\text{Ta}_{1-x}\text{O}_4$, where x is 0 to 0.20;
- (c) $\text{Y}_{1-y}\text{Tm}_y\text{TaO}_4$, where y is 0 to 0.03;
- (d) a solid solution of (a) and (b);
- (e) a solid solution of (a) and (c);
- (f) $\text{Y}_{1-y}\text{Tb}_y\text{TaO}_4$, where y is 0.001 to 0.15;
- (g) $\text{Lu}_{1-y}\text{Tb}_y\text{TaO}_4$, where y is 0.001 to 0.15;
- (h) $\text{Gd}_{1-y}\text{Tb}_y\text{TaO}_4$, where y is 0.001 to 0.15;

- (i) a solid solution of at least two of (f), (g) and (h);
 (j) any of (a) to (i) wherein up to 45 mole percent of the yttrium, lutetium or gadolinium is replaced by lanthanum;
 (k) any of (a) to (i) wherein up to 15 mole percent of the yttrium, lutetium or gadolinium is replaced by ytterbium; and
 (l) any of (a), (b), (c), (d) and (e) wherein up to 15 mole percent of the yttrium or lutetium is replaced by gadolinium;
 the process comprising
 (a) intimately mixing stoichiometric quantities of corresponding precursor oxides;
 (b) mixing the resultant mixture with a flux capable of producing an alkali metal oxide;
 (c) firing the flux-containing mixture in an inert container in the range of 1100 °C to 1400 °C for at least 3 hours; and
 (d) recovering the phosphor;
 characterized in that the flux of step (b) also contains 0.1 to 1.0% of an alkali metal metasilicate.
2. A process according to Claim 1 wherein the total flux mixture is present in 30% to 60% by weight based on the total weight of the precursor oxide.
 3. A process according to Claim 2 wherein the flux capable of producing an alkali metal oxide is selected from the group consisting of alkali metal sulfates, phosphates and carbonates.
 4. A process according to Claim 2 wherein the flux mixture comprises lithium sulfate and lithium metasilicate.
 5. A process according to Claim 1 wherein steps (a) and (b) are combined.
 6. A process according to Claim 2 wherein the alkali metal metasilicate component of the flux is present in an amount of 0.1% to 1.0% based on the total weight of precursor oxide.
 7. A process according to Claim 2 wherein the phosphor is a terbium activated yttrium tantalate.
 8. A process according to Claim 2 wherein the phosphor is thulium activated yttrium tantalate.
 9. A process according to Claim 2 wherein the phosphor is niobium activated yttrium tantalate.
 10. An X-ray intensifying screen made from the phosphor prepared according to Claim 2.

Patentansprüche

1. Verfahren zur Herstellung eines Leuchtstoffs mit verbessertem Röntgenstrahlungs-Wirkungsgrad und verbesserter Reinheit, hergestellt aus einem Tantalat-Leuchtstoff der monoklinen M'-Struktur, ausgewählt aus der aus
 - (a) $\text{YNb}_x\text{Ta}_{1-x}\text{O}_4$, worin x 0 bis 0,15 ist;
 - (b) $\text{LuNb}_x\text{Ta}_{1-x}\text{O}_4$, worin x 0 bis 0,20 ist;
 - (c) $\text{Y}_{1-y}\text{Tm}_y\text{TaO}_4$, worin y 0 bis 0,03 ist;
 - (d) einer festen Lösung von (a) und (b);
 - (e) einer festen Lösung von (a) und (c);
 - (f) $\text{Y}_{1-y}\text{Tb}_y\text{TaO}_4$, worin y 0,001 bis 0,15 ist;
 - (g) $\text{Lu}_{1-y}\text{Tb}_y\text{TaO}_4$, worin y 0,001 bis 0,15 ist;
 - (h) $\text{Gd}_{1-y}\text{Tb}_y\text{TaO}_4$, worin y 0,001 bis 0,15 ist;
 - (i) einer festen Lösung von wenigstens zweien der Stoffe (f), (g) und (h);
 - (j) irgendeinem der Stoffe (a) bis (i), worin bis zu 45 Mol-% des Yttriums, Lutetiums oder Gadoliniums durch Lanthan ersetzt sind,
 - (k) irgendeinem der Stoffe (a) bis (i), worin bis zu 15 Mol-% des Yttriums, Lutetiums oder Gadoliniums durch Ytterbium ersetzt sind; und
 - (l) irgendeinem der Stoffe (a), (b), (c), (d) und (e), worin bis zu 15 Mol-% des Yttriums oder Lutetiums durch Gadolinium ersetzt sind,
 bestehenden Gruppe, wobei das Verfahren

- (a) das innige Vermischen stöchiometrischer Mengen der entsprechenden Vorstufen-Oxide;
 (b) das Vermischen der resultierenden Mischung mit einem Flußmittel, das zur Erzeugung eines Alkalimetalloxids befähigt wird;
 (c) das Brennen der flußmittelhaltigen Mischung in einem inerten Behälter im Bereich von 1100 °C bis 1400 °C während wenigstens 3 h; und
 (d) das Isolieren des Leuchtstoffs;
 umfaßt, dadurch gekennzeichnet, daß das Flußmittel aus Schritt (b) ebenfalls 0,1 bis 1,0 % eines Alkalimetallmetasilicats enthält.
2. Verfahren nach Anspruch 1, worin das gesamte Flußmittel-Gemisch in einer Menge von 30 bis 60 Gew.-%, bezogen auf das Gesamt-Gewicht der Vorstufen-Oxide, vorliegt.
3. Verfahren nach Anspruch 2, worin das zur Erzeugung eines Alkalimetalloxids befähigte Flußmittel aus der aus Alkalimetallsulfaten, -phosphaten und -carbonaten bestehenden Gruppe ausgewählt ist.
4. Verfahren nach Anspruch 2, worin das Flußmittel Lithiumsulfat und Lithiummetasilicat umfaßt.
5. Verfahren nach Anspruch 1, worin die Schritte (a) und (b) kombiniert werden.
6. Verfahren nach Anspruch 2, worin die Alkalimetallmetasilicat-Komponente des Flußmittels in einer Menge von 0,1 % bis 1,0 %, bezogen auf das Gesamt-Gewicht der Vorstufen-Oxide, vorliegt.
7. Verfahren nach Anspruch 2, worin der Leuchtstoff ein durch Terbium aktiviertes Yttriumtantalat ist.
8. Verfahren nach Anspruch 2, worin der Leuchtstoff ein durch Thulium aktiviertes Yttriumtantalat ist.
9. Verfahren nach Anspruch 2, worin der Leuchtstoff ein durch Niob aktiviertes Yttriumtantalat ist.
10. Röntgenstrahlungs-Verstärkungsschirm, gefertigt aus dem nach Anspruch 2 hergestellten Leuchtstoff.

Revendications

1. Procédé pour la préparation d'un phosphore ayant de meilleures pureté et efficacité vis-à-vis des rayons X, préparé à partir d'un phosphore au tantalate ayant la structure monoclinique M' choisie dans le groupe consistant en :
- (a) $\text{YNb}_x\text{Ta}_{1-x}\text{O}_4$, dans lequel x est 0 à 0,15;
 (b) $\text{LuNb}_x\text{Ta}_{1-x}\text{O}_4$, dans lequel x est 0 à 0,20;
 (c) $\text{Y}_{1-y}\text{Tm}_y\text{TaO}_4$, dans lequel y est 0 à 0,03;
 (d) une solution solide de (a) et (b);
 (e) une solution solide de (a) et (c);
 (f) $\text{Y}_{1-y}\text{Tb}_y\text{TaO}_4$, dans lequel y est 0,001 à 0,15;
 (g) $\text{Lu}_{1-y}\text{Tb}_y\text{TaO}_4$, dans lequel y est 0,001 à 0,15;
 (h) $\text{Gd}_{1-y}\text{Tb}_y\text{TaO}_4$, dans lequel y est 0,001 à 0,15;
 (i) une solution solide d'au moins deux des (f), (g) et (h);
 (j) l'un quelconque des (a) à (i) dans lequel jusqu'à 45% en moles d'yttrium, lutétium ou gadolinium sont remplacés par du lanthane;
 (k) l'un quelconque des (a) à (i) dans lequel jusqu'à 15% en moles d'yttrium, lutétium ou gadolinium sont remplacés par l'ytterbium;
 (l) l'un quelconque des (a), (b), (d) et (e) dans lequel jusqu'à 15% en moles d'yttrium ou lutétium sont remplacés par du gadolinium;
- le procédé comprenant:
- (a) le mélange étroit de quantités stoechiométriques des oxydes précurseurs correspondants;
 (b) le mélange du mélange résultant avec un fondant capable de produire un oxyde de métal alcalin;
 (c) la calcination du mélange contenant le fondant dans un récipient inerte à une température comprise dans la gamme de 1100 °C à 1400 °C pendant au moins 3 heures; et
 (d) la récupération du phosphore;
- caractérisé en ce que le fondant de l'étape (b) contient aussi 0,1 à 1,0% d'un métasilicate de métal alcalin.

2. Procédé suivant la revendication 1, dans lequel le mélange total de fondants est présent en une proportion de 30% à 60% en poids par rapport au poids total des oxydes précurseurs.
- 5 3. Procédé suivant la revendication 2, dans lequel le fondant capable de produire un oxyde de métal alcalin est choisi dans le groupe consistant en sulfates, phosphates et carbonates de métal alcalin.
4. Procédé suivant la revendication 2, dans lequel le mélange de fondants comprend du sulfate de lithium et du métasilicate de lithium.
- 10 5. Procédé suivant la revendication 1, dans lequel les étapes (a) et (b) sont combinées.
6. Procédé suivant la revendication 2, dans lequel le composant métasilicate de métal alcalin du fondant est présent en une quantité de 0,1% à 1,0% par rapport au poids total des oxydes précurseurs.
- 15 7. Procédé suivant la revendication 2, dans lequel le phosphore est un tantalate d'yttrium activé par du terbium.
8. Procédé suivant la revendication 2, dans lequel le phosphore est un tantalate d'yttrium activé par du thulium.
- 20 9. Procédé suivant la revendication 2, dans lequel le phosphore est un tantalate d'yttrium activé par du niobium.
10. Ecran intensifiant les rayons X fabriqué à partir du phosphore préparé suivant la revendication 2,
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FIG. 1

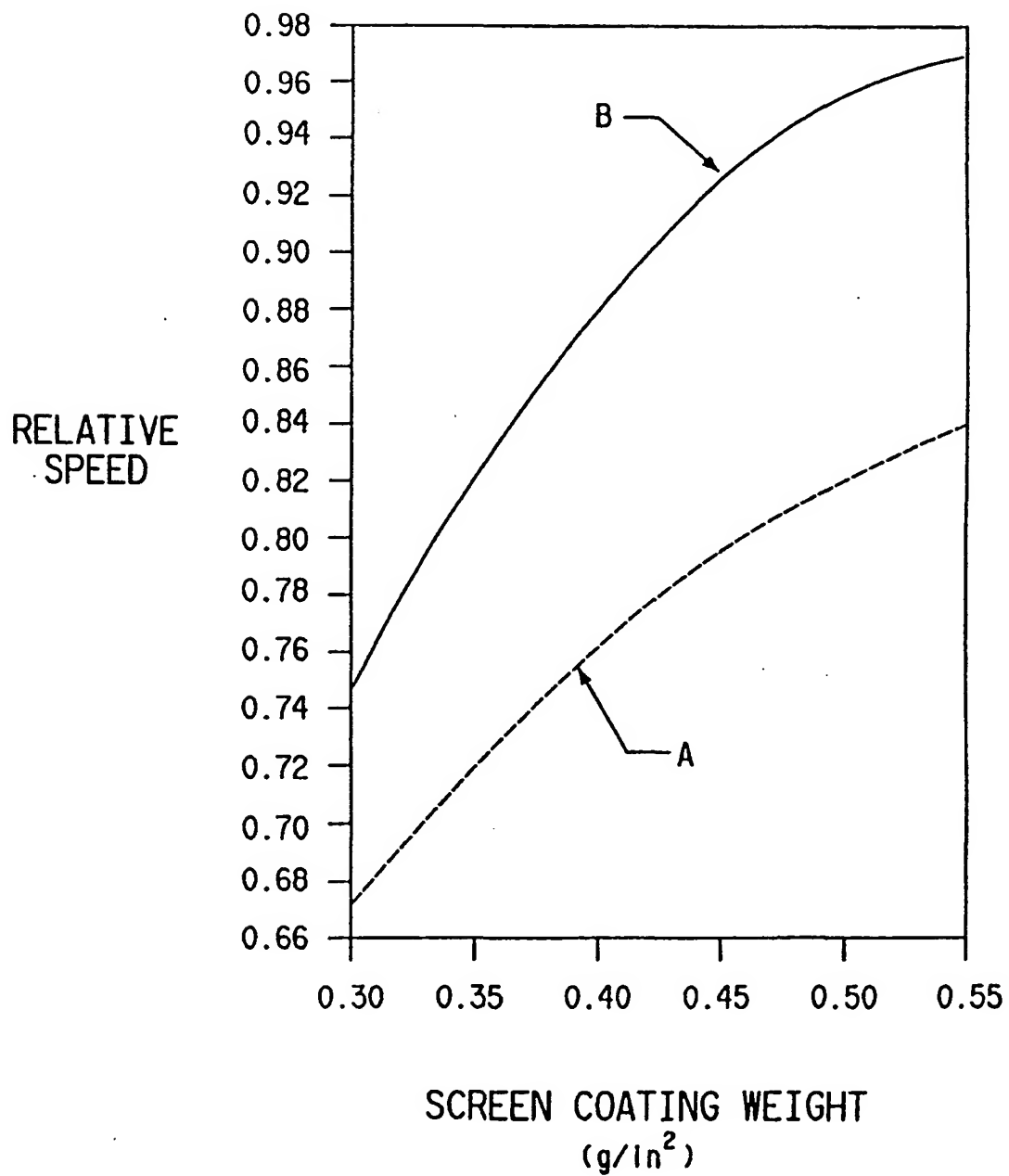


FIG.2

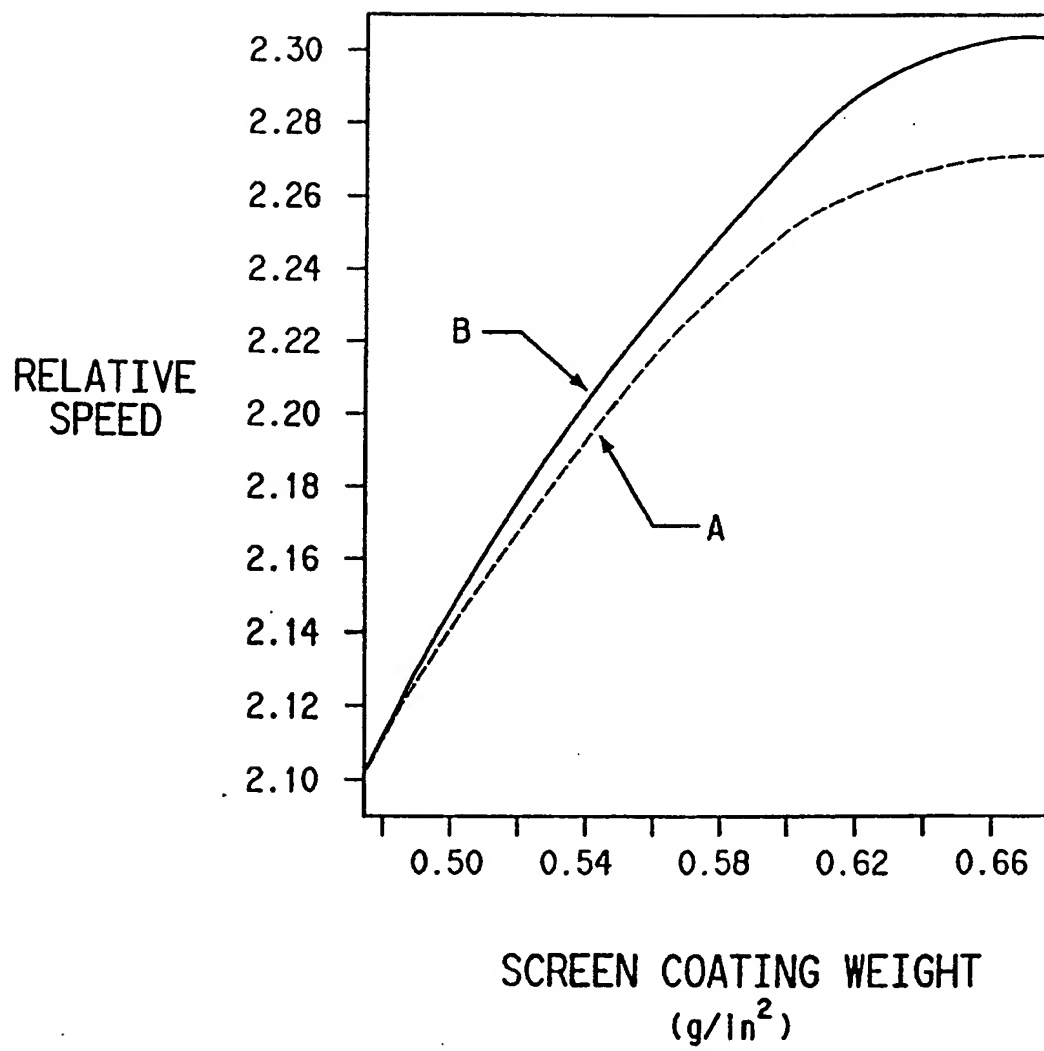


FIG.3

